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LITERATURE SURVEY OF EMISSIONS ASSOCIATED WITH EMERGING ENERGY TECHNOLOGIES

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Quantitative estimates of criteria air pollutant emissions from energy-related operations are tabulated. A broad spectrum of sulfur-containing compounds, nitrogen-containing compounds, and hydrocarbons has been identified from analyses of intermediate process streams and final products from fuel conversion processes. The surveyed literature provides a basis for identifying the major emissions. The same or similar species are expected to be emitted from each fuel conversion facility.

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Quantitative estimates of criteria air pollutant emissions from energy-related operations are tabulated. A broad spectrum of sulfur-containing compounds, nitrogen-containing compounds, and hydrocarbons has been identified from analyses of intermediate process streams and final products from fuel conversion processes. The surveyed literature provides a basis for identifying the major emissions. The same or similar species are expected to be emitted from each fuel conversion facility. These compounds are listed as follows:

- Sulfur-containing compounds will include SO_2, H_2S, thiols, sulfides, and thiophenes.
- Nitrogen-containing compounds will include NO, NO_2, NH_3, HCN, and heterocycles.
- Organic compounds will include primarily volatile hydrocarbons up to C_{10}. Other organics such as aldehydes, ketones, phenols, and POM are expected. The carcinogenicity of various POM presents an additional airborne hazard.

The extent to which any of these species is released to the atmosphere depends to a large degree on currently undefined processing details.

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SECTION 1
INTRODUCTION

PURPOSE

The growing demand for energy coupled with the shortage of domestic gas and liquid fuels has resulted in the emergence of new processes and technologies aimed at producing energy from domestically available fossil fuels. The ultimate goal must be to meet the increasing energy demand in environmentally acceptable ways. Operations such as coal gasification and liquefaction, shale oil production, and petroleum refining will assume an increased role in future energy production. It is therefore necessary to assess the potential impact of these processes on air quality.

The purpose of this task is to perform a literature survey to gather information on the composition and rates of emissions of organic, nitrogen-containing and sulfur-containing constituents from the following types of energy-related operations:

1. Coal gasification,
2. Coal liquefaction,
3. Shale oil production, and
4. Petroleum refining.

ORGANIZATION

This report is organized into three sections. The first section is an overall introduction to the report.

The second section deals with fuel contaminants in coal, coal liquefaction products, shale oil, and petroleum. A discussion is presented on the relative amounts and the chemical form of sulfur and nitrogen in each type of fuel.

The third section provides a brief description of each of the four classes of conversion processes. Emissions estimates are summarized and, as the literature permits, the identities and concentrations of compounds associated with the various processes are tabulated.

BACKGROUND

The United States depends on coal, petroleum liquids, petroleum gases, hydroelectricity, and nuclear power for 89 percent of its energy (ref. 1). Petroleum and natural gas supply approximately 75 percent of this requirement. These fuels are in short supply and are projected to decline rapidly in the face of a growing demand, which has pushed U.S. dependence on foreign oil from 15 percent of the domestic oil consumption in 1973 during the peak of the "energy crisis" to 40 percent by mid-1976. Fortunately, the United States has an abundant supply of coal, which is in excess of 600 billion tons of remaining mineable reserves and over 3,300 billion tons of total coal resources. Domestic coal reserves, compared to reserves of other fuels, are five times the shale reserves, over 13 times the oil reserves, and almost 19 times the natural gas reserves (ref. 2). It is, therefore, understandable that new emphasis is being placed on the development of technologies for the environmentally acceptable utilization of coal. These technologies include improved mining techniques, coal gasification, coal liquefaction, shale oil production, and improved techniques for fuel combustion and power generation.

Coal utilization is expected to double between 1975 and 1985. The Federal Power Commission estimates that coal gasification plants will supply 0.3×10^{15} Btu by 1980 and approximately 3.2×10^{15} Btu by 1990 (ref. 3). This translates into 36 coal gasification plants producing 250×10^{6} CFD of high Btu substitute natural gas (SNG) by 1990. In addition, if the goals of Project Independence are to be met, the 41 energy facilities listed in Table I must be built immediately, and as many as 165 synthetic fuel plants will be required by 1985 to compensate for decreasing domestic natural gas supplies and to reduce the dependence on imported oil. The resulting environmental impact of this number of facilities could be substantial, even with environmental controls.

TABLE 1. SYNTHETIC FUEL PLANTS RECOMMENDED FOR PROJECT INDEPENDENCE (REF. 3)

Number of plants	Product	Quantity (per plant)
16	Low-Btu gas from coal as fuel for power generation	800-1,000 MW of electricity
12	High-Btu gas from coal	250 x 10^6 CFD[a]
6	Syn-crude, motor fuel, steam distillate fuel oils, and/or deashed coal from coal	100,000 BPD[b]
5	Shale oil	100,000 BPD
2	Fuel grade methyl alcohol from coal	50,000 TPD[c]
Total 41		

[a]CFD = cubic feet per day.
[b]BPD = barrels per day.
[c]TPD = tons per day.

SECTION 2
FUEL CONTAMINANTS

The technology for coal liquefaction and shale oil production is poorly defined. Although commercial coal gasifiers are in operation outside this country, no large-scale commercial domestic facilities are operating at present. The identity and rates of gaseous emissions from these processes are often based on pilot or demonstration plant operations and are all too frequently based on no more than engineering estimates. While petroleum-refining technology is well defined, reported emissions rates and compositions are limited. The literature has, at best, revealed pollutant emissions estimates for five of the criteria pollutants: particulates, SO_2, CO, hydrocarbons, and NO_x. In view of this significant data gap, the literature was further examined for information on the molecular form of sulfur and nitrogen contaminants in various raw and refined fuels. An understanding of the chemical form of fuel contaminants may provide a better basis for gaining insight into the transformations of the contaminants and the form of the resulting emissions from various conversion processes.

Coal, liquid coal product, shale oil, and petroleum crude oil contain three types of contaminants: sulfur, nitrogen, and trace elements. This discussion will be limited to the sulfur and nitrogen compounds. The primary source for the information in this section is a review of fuel contaminant literature by Massey et al. (ref. 4).

Table 2 illustrates typical elemental analyses of eight selected fuels and allows a comparison of their sulfur and nitrogen content. Table 3 provides a breakdown of the qualitative distribution of sulfur and nitrogen in fuels and allows a comparison with other fuels. This suggests that a portion of the sulfur and most of the nitrogen originate from organic sulfur and nitrogen compounds common to all fuels.

TABLE 3. ELEMENTAL ANALYSIS OF TYPICAL FUELS (REF. 4)

	Weight percent						H/C (atomic)
	C	H	O	N	S	Ash	
Coal (mf)							
Subbituminous (Big Horn)	69.2	4.7	17.8	1.2	0.7	6.5	0.81
Bituminous (Pittsburgh)	78.7	5.0	6.3	1.6	1.7	6.9	0.76
Coal liquids (Big Horn)	88.2	8.9	1.03	0.4	0.04	<1	1.20
(Pittsburgh)	89.1	8.5	1.5	0.6	0.3	<1	1.10
Shale oil	80.7	10.4	5.9	2.3	1.1		1.55
Petroleum crude (Pennsylvania)	85	14	1	1	1	<1	1.98
Residual oil[a]	86.6	12.5	0	0.31	0.89	0.03	1.74
Distillate oil[a]	86.9	13.1	0	0.03	0.10	<0.002	1.81

[a]Ref. 5

COAL

Complex hypothetical molecular structures have been proposed for coal (ref. 6). These models illustrate the predominantly aromatic character of coal. Table 4 summarizes selected typical chemical and physical properties for the major rank classes of coal. The aromatic character of coal increases with rank. Other parameters such as sulfur, nitrogen, and mineral-matter contents, and type of mineral matter do not vary systematically with rank.

Coal is a complex material and may be viewed as a warehouse for myriad organic species. Lowry (ref. 9) has listed 348 compounds, and Andersen and Wu (ref. 10) have provided data on 833 compounds identified in the products of coal carbonization. More recently (ref. 11) 133 compounds consisting of paraffins, olefins, and neutral heterocycles were identified in low-temperature bituminous coal tar.

Sulfur is present in coal as both organic and inorganic species. The inorganic sulfur occurs as pyritic or sulfide sulfur and as sulfate sulfur. Although these figures are highly variable, approximately half the total sulfur in coal occurs as pyritic sulfur while sulfate typically accounts for only 0.1 percent.

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Organic sulfur in coal occurs in four forms: mercaptans, sulfides, disulfides, and thiophene-based compounds. These same four classes of compounds have been found in crude oils. Selected examples of sulfur compounds with boiling points less than 200° C are presented in Table 3 from analyses of coal products. The fractional distribution of these compounds in coal itself is poorly defined.

Nitrogen contaminants in fuels have not been as well characterized as sulfur compounds. Nitrogen is present in coal as an integral part of its aromatic chemical structure. Indirect evidence suggests that nitrogen occurs as pyridines, quinolines, acridines, pyrroles, indoles, carbazoles, and porphyrins (ref. 4). The fractional distribution of the nitrogen compounds in coal is largely unknown.

COAL LIQUID

Coal is liquefied by processes utilizing pyrolysis, solvent extraction, and catalytic or noncatalytic hydrogenation. The liquid product may contain organic nitrogen and sulfur originally present as organic contaminants of coal. The inorganic sulfur in the parent coal, primarily sulfides, is converted to hydrogen sulfide during liquefaction. The contaminant level in the liquid product depends on the severity of the product-upgrading processes (hydrotreating).

Elemental analyses of parent coal and liquid products from pilot operations are presented for comparison in Table 6. Table 3 allows a comparison of the qualitative distribution of sulfur and nitrogen contaminants in coal liquids with that of other fuels. The liquid product typically contains less than 1% sulfur. Thirteen thiophene derivatives and one disulfide were identified in a sample of noncatalytically hydrogenated liquid product (ref. 4). In addition, 8 organosulfur compounds and over 40 sulfur compounds have been observed in respective GLC profiles of COED oil and Synthoil oil (ref. 12).

The nitrogen contaminants of liquid coal product are anticipated to be similar to those previously listed for coal and coal tars.* Indole and skatole have been recently identified in Synthoil oil (ref. 12).

*The expected nitrogen compounds include pyridines, quinolines, acridines, pyrroles, indoles, carbazoles, and benzamides.

TABLE 9: SELECTED ORGANIC SULFUR COMPOUNDS PRESENT IN COAL PRODUCTS

Formula	Name	Structure	B.P., °C	Occurrence in coal product
Thiols (mercaptans)		(RSH)		
CH_4S	Methanethiol	CH_3SH	6	Coal gas
C_2H_6S	Ethanethiol	C_2H_5SH	35	Tar, benzole
C_6H_6S	Benzenthiol		169.1	H.T. tar[a]
$C_{14}H_{10}S$	Anthracenthiol			Coal oil
Alkyl sulfides (thioethers)		(RSR')		
C_2H_6S	Methyl sulfide	$(CH_3)_2S$	37.3	Benzole
$C_4H_{10}S$	Ethyl sulfide	$(C_2H_5)_2S$	91.1	Benzole
Disulfides		(RSSR')		
$C_2H_6S_2$	Methyl disulfide	$CH_3{\cdot}S{\cdot}S{\cdot}CH_3$	116	Coal gas
$C_6H_6S_2$	p-Dithiokol		77	Tar
Thiophene and derivatives				
C_4H_4S	Thiophene		84.1	Tar, benzene, coal oil
C_5H_6S	2-Methylthiophene		112.5	Crude toluene
C_6H_8S	2-5 Dimethyl thiophene		131.6	Tar
$C_7H_{10}S$	2,4-Trimethyl thiophene		170.6	Tar, light[b] oil, benzole
$C_8H_{12}S$	Tetramethyl thiophene		188; 184	L.T. tar
C_4H_8S	Tetrahydro-thiophene		121	L.T. tar; pyridine

[a] H.T. = High temperature.
[b] L.T. = Low temperature.

TABLE 6. PROPERTIES OF COAL LIQUEFACTION PRODUCTS[a] AND OF PARENT COAL

Fuel	Weight %						Higher heating value	Ref
	C	H	O	N	S	Ash	MJ/kg (Btu/lb)	
COED syncrude	87.1	10.8	1.6	0.3	0.1	<0.01	NS	14
COED char	75.4	0.8	1.0	1.0	5.4	20.3	11,040	
Illinois no. 6 coal	67.0	4.8	10.9	1.3	4.1	12.1	12,150	
Garrett tar	83.7	6.3	0.8	1.8	0.6	NS	NS	16
Garrett char	74.0	1.9	3.9	1.0	0.6	18.6	11,700	
Big Horn coal	68.8	4.3	15.5	1.0	0.8	9.9	9,300	
Gulf	90.6	8.2	0.8	0.4	<0.03	NS	NS	17
Big Horn coal	69.3	4.6	18.9	1.2	0.3	5.4	8,730	
Syncrude (HS)	89.3	8.9	1.0	0.4	0.04	71.0	NS	4
Big Horn coal	69.3	4.7	17.8	1.2	0.7	5.3	NS	
Syncrude (MS)	89.1	8.7	1.3	0.8	0.2	71.0	NS	4
Pittsburgh coal	78.7	5.0	6.3	1.6	1.7	6.9	NS	
H-COAL syncrude	NS	9.5	NS	0.7	0.3	NS	18,390	18
H-COAL fuel oil	NS	8.4	NS	1.1	0.4	NS	NS	
Illinois no. 6	71.7	5.4	8.1	1.0	3.0	9.9	NS	
HRI-synthoil	88.0	9.1	NS	0.6	0.2	1.0	17,700	19
Kentucky	NS	NS	NS	NS	4.8	NS	NS	
HRI-synthoil Middle Kittanning No. 6	87.4	7.3	1.6	0.9	0.3	1.3	16,840	19
	NS	NS	NS	NS	3.0	NS	0,000	
PAMCO-EDS	86.0	5.9	3.1	1.2	0.7	0.2	16,250	20
Kentucky coal	71.6	5.0	8.8	1.4	3.6	9.1	12,900	
Exxon-EDS (Naphtha)	86.8	13.9	0.2	0.08	0.005	NS	19,300	21
Exxon-EDS (Fuel oil)	90.8	8.6	0.3	0.2	0.04	NS	18,100	
Illinois no. 6	69.6	5.1	9.3	1.8	4.3	9.8	12,814	

[a]Properties depend on severity of hydrogenation.
NS = Not specified.

TABLE 7. COMPOSITION OF TOTAL AROMATIC FRACTION OF LIQUID COAL (REF. 13)

Compound type	Volume %
Tetrahydrophenanthrenes	16.3
Pyrenes/fluoranthenes	16.1
Hexahydropyrenes	15.3
Dihydropyrenes	10.3
Octahydrophenanthrenes	9.6
Decahydropyrenes	7.9
Phenanthrenes	6.3
Tetralins	4.9
Tetrahydrofluoranthenes	4.6
Chrysenes	3.9
Benzopyrenes	3.0
Tetrahydrobenzonaphthenes	0.7
Benzenes	0.2

The results from mass spectral analysis of the total aromatic fraction of a coal liquid is presented in Table 7. The liquid was produced by catalytic hydrogenation of Big Horn subbituminous coal. Complete resolution of the various fractions of the liquid were not reported; however, synthetic crude derived from the pyrolysis (COED) of coal yielded 49% (vol) aromatics, 41% naphthenes, 10% paraffins, and 0% olefins (ref. 14). In addition to these results, polynuclear aromatic hydrocarbons (PAH) have also been identified and quantified in various liquid products from pilot COED and Synthoil operations (ref. 15).

SHALE OIL

Oil shale is a type of sedimentary rock that is rich in organics. Considerable quantities of oil (shale oil) are released on subjecting this shale to destructive distillation in a closed retort system. Table 3 may be used to compare a typical elemental analysis of shale oil with analyses of other fuels.

Crude shale oil from the retort typically has 0.6 to 1.1% (wt) sulfur and 1.1 to 2.3% (wt) nitrogen (refs. 7, 4). Table 2 allows a comparison of the qualitative distribution of sulfur and nitrogen contaminants in shale oil with that of other fuels. Shale oil generally has higher concentrations of nitro-

gen contaminants than petroleum crudes; in addition, the ratio of olefins to paraffins is also higher.

Analysis of the naphtha fraction of Colorado shale oil for sulfur compounds revealed 75% thiophenes, 19% sulfides, 3% disulfides, and 4% thiols (ref. 6). The literature provides qualitative identification of 33 thiophenes, 3 thiols, 3 disulfides, 1 trisulfide, and 2 cyclic sulfides. Sulfur analysis of the gas oil fraction of Colorado shale oil has indicated the presence of thiophenes, benzothiophenes, and more complex compounds.

Analysis of the naphtha fraction of Colorado shale oil for nitrogen compounds revealed 31 pyridines, 5 pyrroles, and 6 nitriles (ref. 6). In the gas oil fraction 33 percent of the nitrogen occurs as single-ring compounds, mainly pyridines; 35 percent occurs as double-ring compounds, e.g., indoles, quinolines, and tetrahydroquinolines; and the remaining 40 percent as multiring compounds. In addition, several porphyrins have also been identified.

PETROLEUM CRUDE

Petroleum crude oil contains primarily hydrocarbons and has relatively uniform contents of carbon (83-87 percent wt) and hydrogen (10-14 percent wt) (ref. 4). Crude oils are mixtures of paraffinic, naphthenic, and aromatic hydrocarbons. Sulfur, nitrogen, and oxygen impurities typically range from 1 to 3 percent. Table 3 may be used to compare an elemental analysis of petroleum crude with those of other fuels.

The location and history of the petroleum formation affect the quality of the petroleum crude. Pennsylvania crudes are principally paraffinic, whereas California crudes are naphthenic in nature. Pennsylvania and midcontinent crudes may contain less sulfur than the heavier southern and western crudes. Within a given crude, both sulfur and nitrogen compounds are concentrated in the heavier fractions, principally in the resins and asphaltenes. Table 3 allows a comparison of the qualitative distribution of sulfur and nitrogen contaminants in petroleum crude with that of other fuels.

The sulfur content of most crudes ranges from 0.1 to 3 percent. The frequency distribution of sulfur content of U.S. crudes from 291 fields is presented in Figure 1. Sulfur has been identified in crude oils as thiols (mercaptans), alkyl sulfides, and heterocycles. Table 8 depicts the fractional distribution of sulfur in various crude oils. Alkyl thiols and alkyl sulfides with both normal and branched alkyl groups have been identified

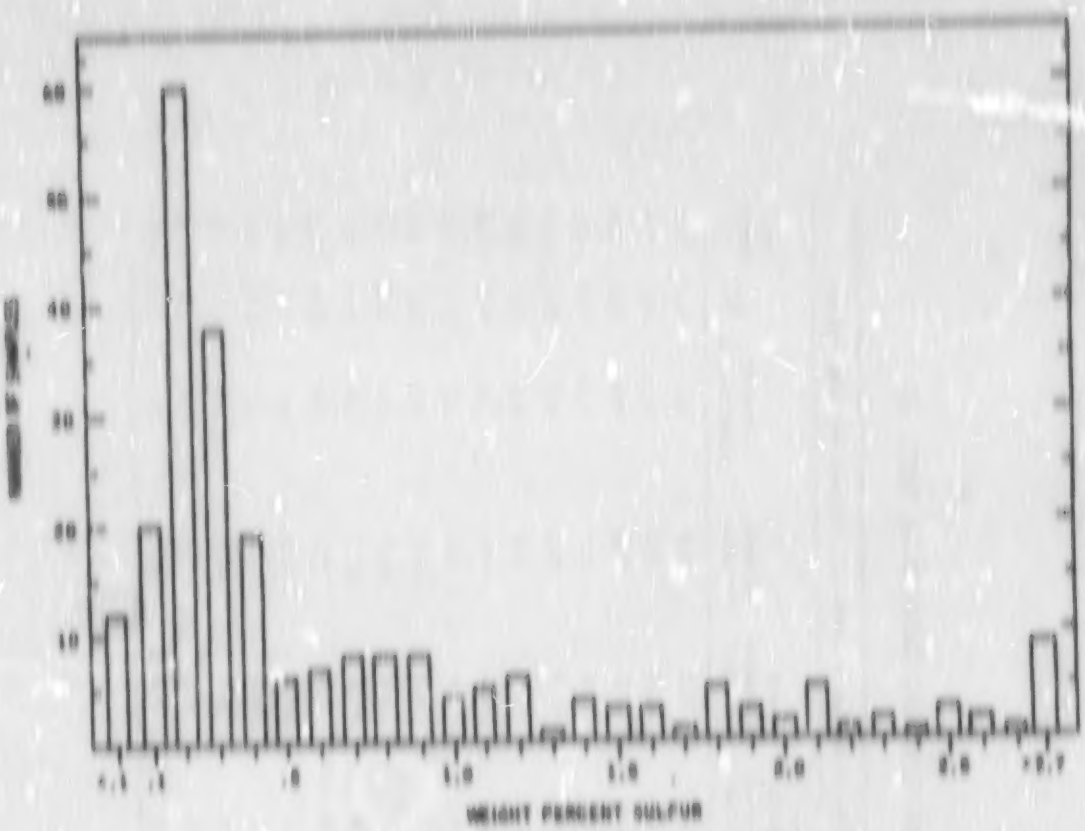

Figure 1. Frequency distribution of sulfur content in crude oils of U.S. giant oil fields (ref. 15).

in petroleum crudes (ref. 4). Cycloalkyl thiols with cyclopentane or cyclohexane rings are found. Cyclic sulfides with at least four or five carbons in the ring structure are also present. The heterocyclic sulfur compounds found in the heavier fractions of crudes have thiophenes, thiaindans, and thienothiophenes as basic building blocks. Analysis of a narrow cut (200-250° C) of Wasson crude has revealed 22 benzo(B)thiophenes, 18 thiaindans, 8 thienothiophenes, and 4 alkyl sulfides.

Nitrogen contamination of petroleum is typically less than 1 percent. Figure 2 illustrates the frequency distribution of nitrogen content of U.S. crudes from 229 fields. Table 8 allows comparison of nitrogen levels in various crudes. The types of nitrogen compounds found in crude oil are listed in Table 9.

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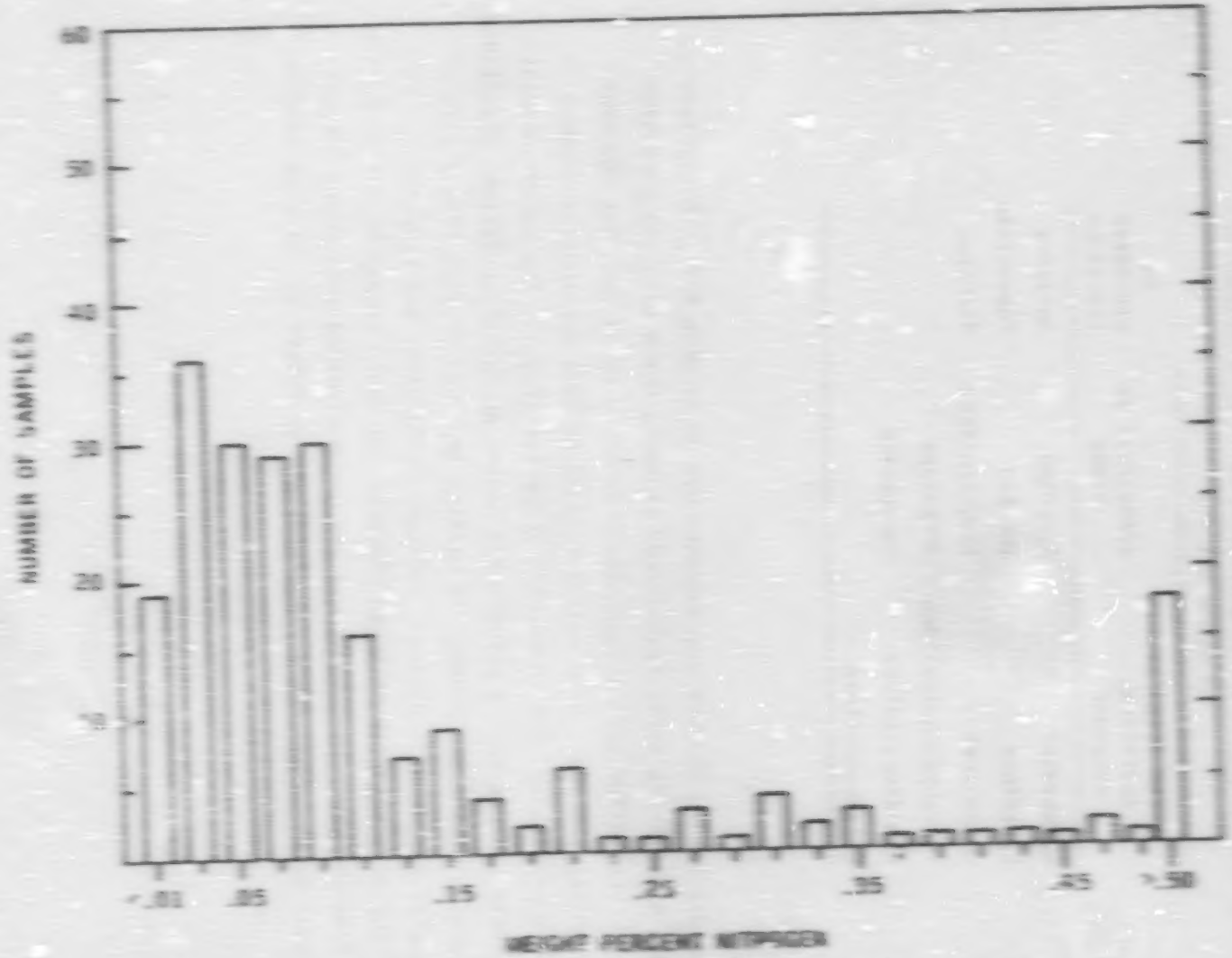

Figure 1. Frequency distribution of nitrogen content in crude oils of U.S. giant oil fields (ref. 15)

TABLE 9. NITROGEN COMPOUNDS IN PETROLEUM (REF. ()

Types of nitrogen compounds found		
In crude oil		
Identified as individual compound	Identified as class	In processed fractions
Carbazoles	Pyrroles	Anilines
Pyridines	Indoles	Phenazines
Quinolines	Isoquinolines	Nitriles
Tetrahydroquinolines	Acridines	
Dihydropyridines	Porphyrins	
Benzoquinolines		

OVERVIEW

This discussion on fuel contaminants has dealt with the chemical form of sulfur and nitrogen in coal, liquid coal product, shale oil, and petroleum crude oil. The sulfur and nitrogen found in these fuels are, for the most part, organically bound. Only coal was found to have substantial amounts of inorganic contaminants, and these were as pyrite (FeS_2). The sulfur content of most fuels is less than 5 percent and occurs as thiols, sulfides, disulfides, and thiophenes. Nitrogen content is usually reported at less than 2 percent and occurs as pyridines, pyrroles, indoles, carbazoles, and benzamides. Only a few of the more volatile of these contaminants would create an air pollution problem from the raw fuel. The forms and concentrations that these contaminants assume during clean fuels processing are addressed in the next section.

SECTION 3
EMISSIONS FROM FUEL CONVERSION FACILITIES

GASIFICATION

Coal is a complex material having a molecular weight of around 3,000. When coal is heated in the absence of oxygen, volatile gases and liquids are released, leaving a char. This char can be further heated in the presence of the appropriate amounts of steam and oxygen to form carbon monoxide (CO), hydrogen (H_2), and some methane (CH_4). This process is known as coal gasification.

The objective of coal gasification processes is to convert the solid coal into a clean, gaseous fuel and, under certain conditions, liquid fuels and useful byproducts. Gasification plants may be categorized into three classes.

1. Low-Btu gasifiers produce industrial and utility boiler fuels (150-300 Btu/SCF).
2. Intermediate-Btu gasifiers produce synthesis gas (300-450 Btu/SCF) as feedstock for manufacture of liquid fuels, methanol, ammonia, and other chemicals.
3. High-Btu gasifiers produce substitute natural gas (SNG) (~1,000 Btu/SCF) and other chemicals.

Gasification technology is not new, having been used in Europe as early as the 1840's. Only three gasification facilities are presently in commercial operation in the United States: one employs Wilputte and two employ Weimann-Galusha gasifiers. These plants have small capacities, employ early technology, and produce low Btu fuel gas. Other processes are operating commercially outside this country: Lurgi, Koppers-Totzek, and Winkler. Many additional gasification schemes are in various stages of development. Twenty-two processes have been reviewed for the Electric Power Research Institute (ref. 16); these are listed in Table 10. Several reviews (refs. 3,16,22,23) have described and compared many of these processes and also have reported their current status (ref. 1). A broad spectrum of operating conditions exists for

TABLE 10. COAL GASIFICATION PROCESSES (REF. 16)

Koppers-Totzek	H.W. Kellogg--Molter Salt
U.S. Bureau of Mines--Synthane	U.S. Bureau of Mines--Stirred Bed Gasifier
Lurgi	U.S. Bureau of Mines--Hydrane
Consolidation Coal--CO_2 Acceptor	Battelle--Ash Agglomerating Gasifier
Bituminous Coal Research--Bi-Gas	Westinghouse--Advanced Gasifier
IGT--HYGAS	Brigham Young--Entrained Bed
IGT--U-GAS	Texaco--Partial Oxidation Process
Winkler	Shell--Partial Oxidation Process
Combustion Engineering	Bituminous Coal Research--Fluidized Bed
Foster Wheeler	Applied Technology Corp.--ATGAS
Atomics International--Molten Salt	City College of New York--Squires

the processes under consideration. Table 11 presents a summary of key operating parameters for eight selected coal gasification processes. The type of reactor and the gasification temperature and pressure vary considerably depending on the process and the desired end product.

Most of the first-generation gasification projects slated for introduction in this country are based on the Lurgi process. Construction of five commercial-sized plants will begin as soon as financial difficulties are resolved; this may be as early as 1978. This discussion will, therefore, primarily address the Lurgi process.

After the coal is mined, it is handled and transported to the gasification facility, where it is then cleaned, crushed, dried, and either stored or fed directly via lock hoppers to the gasifier. A generalized flow diagram of a 250 x 10^6 CFD high-Btu SNG facility is shown in Figure 3. The Lurgi gasifier operates as a countercurrent moving-bed reactor at 300-420 psia pressure and 1,100 to 1,700° F and is depicted in Figure 4. The coal is first devolatilized in the top zone of the gasifier at 1,100 to 1,400° F. The remaining char passes into the middle or gasification zone where the carbon and steam react to

TABLE II. [illegible] ([illegible])

Process	Type	Oxidant supplied	Temperature, °F	Pressure, psia	Product gas
[illegible]	Recycled slagging	oxygen	2,700	15	Medium Btu
Synthane	Fluid bed	oxygen	Top—600 Bottom—1,700	1,000	High Btu
Lurgi	Countercurrent bed	oxygen	Top—1,100-1,400 Bottom—2,700	450	High Btu
CO_2 Acceptor	Fluid bed	air[b]	1,500	250	High Btu
H-Coal	Top zone—ebullated Bottom zone—slagging	oxygen	Top zone—1,700 Bottom zone—3,000	1,500	High Btu
HYGAS	Fluid bed 4 sections	oxygen	Top—600 2nd sect.—1,250 3rd sect.—1,750 Bottom—1,900	1,500	High Btu
U-Gas	Fluid bed	air	1,900	350	Low Btu
Winkler	Fluid bed	oxygen	1,700	35	Medium Btu

[a]Values shown in this table depend on the original losses chosen; plant sizes as well as other factors differ and direct comparisons of the values is difficult.

[b]In Acceptor regenerator.

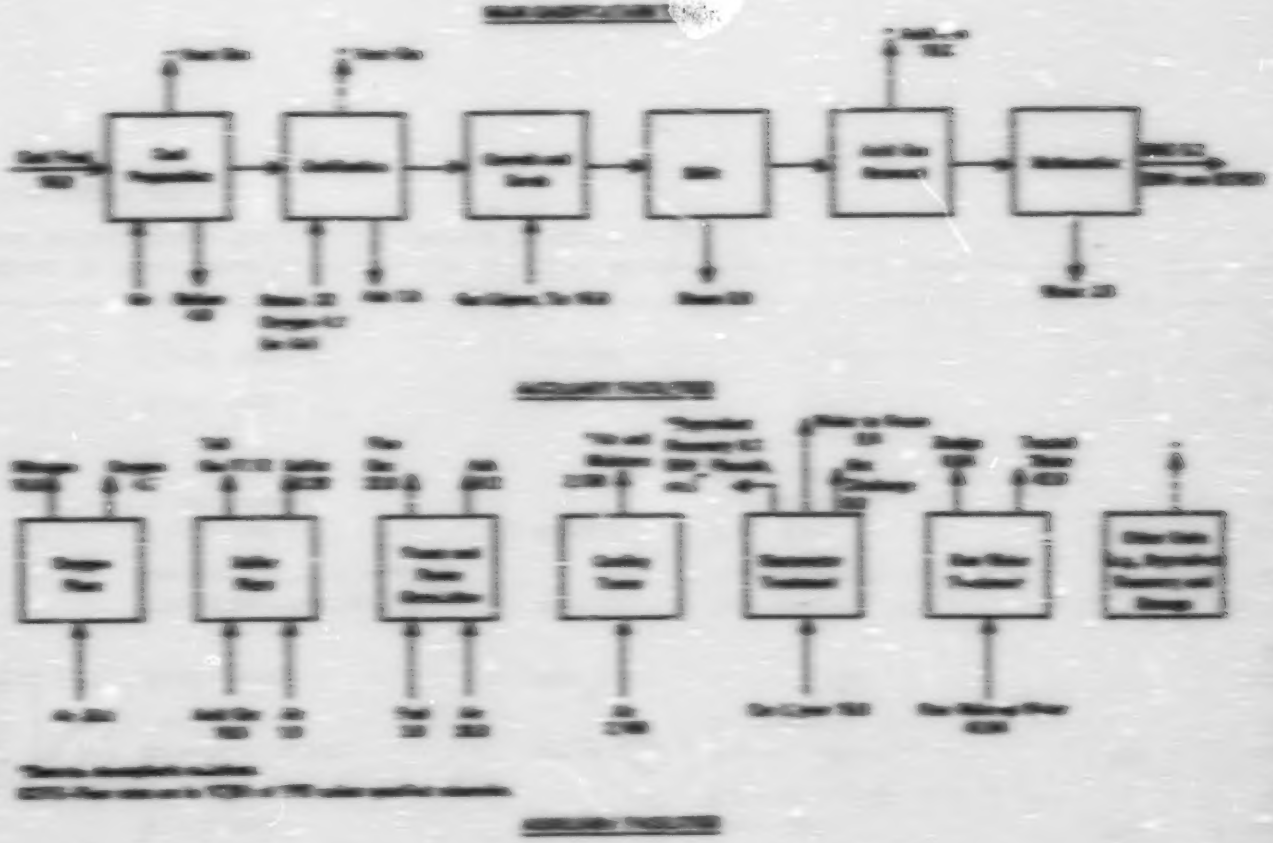

Figure 1. [illegible]

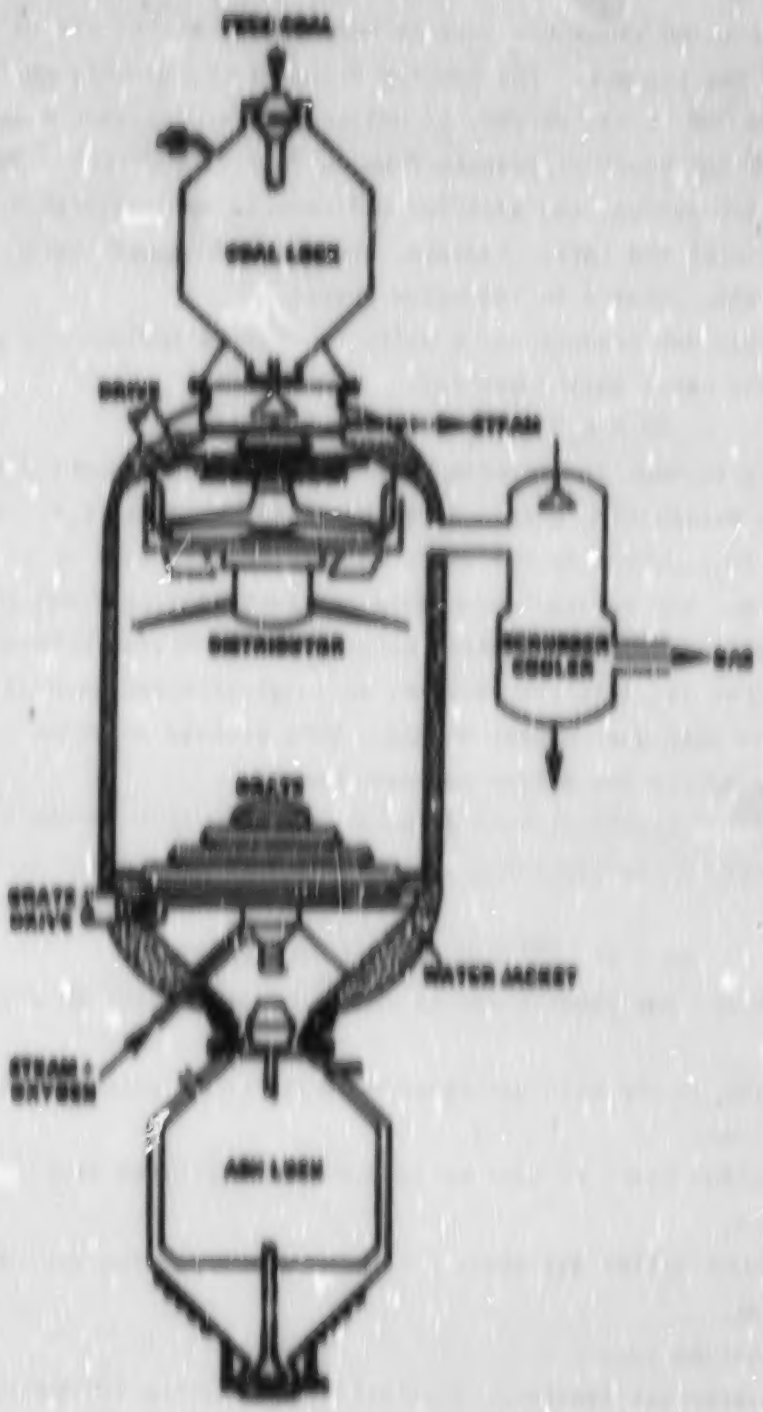

Figure 4. Lurgi gasifier.

produce fuel gas rich in CO and H_2:

$$C + H_2O + 31.4 \text{ kcal/mole} \rightarrow CO + H_2$$

In the lower zone the remaining char is burned with either air or oxygen to supply heat to the process. The heating value of the gasifier product gas will range from 300 to 450 Btu/SCF if oxygen is used, whereas a lower quality product (150 to 300 Btu/SCF) results from an "air blown" unit. Before undergoing further processing, the gasifier effluent is water-quenched and cooled to remove particles and tars. Ammonia, phenols, and other highly soluble compounds are also removed in the water quench.

For high-Btu SNG production, a shift reactor is included to produce hydrogen via the water shift reaction.

$$CO + H_2O \rightarrow CO_2 + H_2 + 9.8 \text{ kcal/mole}$$

The H_2-to-CO ratio must be approximately 3:1 for subsequent product upgrading in the methanation step. After the shift reactor, H_2S, formed in the gasifier, and CO_2, formed in the shift conversion, are removed in the acid gas removal section. The several techniques available for acid gas removal include hot carbonate solutions, amine solutions, and cooled methanol (Rectisol). It is likely that the Rectisol process, an Lurgi-licensed technology, will be employed in the acid gas removal module. This process provides a concentrated H_2S and CO_2 stream to the sulfur recovery module.

The final processing step is methanation where much of the H_2 formed in the shift reactor is catalytically reacted with CO to produce methane and steam.

$$CO + 3H_2 \rightarrow H_2O + CH_4 + 48.2 \text{ kcal/mole}$$

After methanation, the product gas is dried and compressed to pipeline pressure for delivery.

In addition to the main gasification unit, other support and peripheral processes include:

1. A sulfur plant to recover sulfur as a byproduct from the acid gases,
2. A power boiler and steam generator to supply the gasifier with steam,
3. A cooling tower,
4. A wastewater treatment facility with phenolics byproduct recovery,
5. A raw makeup water treatment facility, and

6. An oxygen plant to provide the gasifier with oxygen.

The high-Btu gas from gasification processes must meet product specifications and be of quality similar to natural gas. Anticipated product gas specifications from eight gasification schemes are summarized in Table 12 along with specifications for three types of natural gas. Not all the processes produce SNG, as is indicated by comparison of the specified heating values. The SNG products compare favorably in composition with natural gases and also possess low contaminant levels. Any major air pollutant emissions problems therefore must occur between the gasifier and the final product stage.

In the gasifier much of the sulfur in the original coal is converted to H_2S and COS. Nitrogen from the coal is converted primarily to NH_3 and HCN. It is here that many of the coal contaminants discussed in the fuel contaminants section enter the gas phase. Typical expected analyses of raw gasifier gas are presented in Table 13 for eight gasification processes. The literature reveals few quantitative details on the measured concentration of trace gaseous species in the raw gasifier gas. Reported analyses of raw gas from pilot and commercial gasification facilities are presented in Table 14.

Atmospheric emissions sources for a gasification plant are illustrated in Figure 3. These sources include the following:

1. Coal handling and pretreatment (coal dryer vent),
2. Vent gases from startup, shutdown, and routine charging of the gasifier (lock hopper gases),
3. Acid gas removal (CO_2 vents),
4. Sulfur recovery (tail gas),
5. Catalyst regeneration,
6. Byproduct recovery and storage,
7. Cooling tower (from possible contamination of cooling water by leaks in heat exchange equipment),
8. Wastewater treatment,
9. Steam boilers (power generation) and process heaters and furnaces,
10. Fugitive emissions (at valves, flanges, seals, pumps, compressors, and other equipment).

A summary of the major gasifier and byproduct species of interest is presented in Table 15. An analytical test plan (ref. 30) has been proposed to

TABLE 11. [illegible] OF AN [illegible] NATURAL GAS ANALYSES[a]

Type	Value of product gas, 10^6 Btu/t	Higher heating value (HHV) of product gas, Btu/scf	Pressure of product gas, psia	Gas analysis, volume %						
				CH_4	C_2H_6	N_2	H_2	CO_2	CO	H_2S + COS
Synthetic gas[b]										
Lurgi-Ruhrgas	290	300	350	8.1	1[illegible]	32.6	1.2	5.2	49.9	0.03
Koppers	250	307	1,000	90.5	90	3.6	2.1	3.7	0.1	90
Lurgi	251	311	915	85.9	86	6.8	1.2	2.0	0.1	86
CO_2 Acceptor	263	332	1,000	91.0	91	4.5	0.8	1.3	0.1	91
BI-CS	250	310	1,275	91.8	92	5.1	1.9	1.1	0.1	92
HYGAS	240	1,000	450	95.0	95	0.6	0.2	0.1	0.1	95
I-Gas	790	156	300	4.9	95	33.8	56.6	6.7	22.2	0.025
Wabiz	185	302	75	2.6	95	42.7	1.2	35.1	38.9	0.02
Natural gas[c]										
Sandora	—	907	75	96.0	98	95	1.2	0.8	95	95
Cleveland	—	1,131	75	80.5	18.2	95	1.3	80	95	95
Mt. City, Pa.	—	1,232	75	87.6	11.3	98	1.1	95	95	95

[a]Values shown in this table depend on the original base chosen; plant sizes as well as other factors affect and direct comparison of the values is difficult.

[b]Ref. 11.

[c]Ref. = Not specified.

[d]Ref. 24.

TABLE 13. [illegible] [illegible] [illegible]

| | | |

enable the assessment of the pollution potential of a Lurgi coal gasification facility. This plan, as shown in Table 16, reflects the anticipated distribution of various major air pollutants among the expected sources in a gasification facility.

Emissions estimates have been compiled from environmental impact statements for four Lurgi-based processes and are summarized in Table 17. Since no domestic operational experience is available for the Lurgi process, the lack of consistency among these results may be attributed to different degrees of emissions control expected for the four facilities. Recent estimates (ref 33), shown in Table 18, have categorized the hydrocarbon emissions according to type. The fugitive emissions were estimated by analogy to petroleum refinery operations. The nonmethane hydrocarbon (NMHC) emissions estimate of 1,673 lb/hr falls within the range of NMHC estimates of Table 17. Notice that 28 percent of the estimated hydrocarbon emissions is as NMHC. It should be noted that over 90 percent of these NMHC emissions are olefinic hydrocarbons and are highly photochemically reactive in the presence of NO_x and sunlight.

The major hydrocarbon sources are likely to be vented lock hopper gases and the tail gas (CO_2 rich) stream from the sulfur recovery plant. The potential problem with lock hopper vent gas can be remedied by incineration. This solution may also be applicable to the tail gas stream from the sulfur plant.

Emissions of NO_x could be significant from coal gasification facilities. Nitrogen oxides emissions from gasification facilities are indicated in Table 17 to be low. It has been assumed that the economic incentive to recover another major nitrogen species, ammonia, as a salable byproduct makes it unlikely that ammonia in waste gases and liquids would be burned, flared, or otherwise emitted.

The major source of sulfur emissions is likely to be the sulfur recovery plant. Most of the sulfur in the coal is converted to H_2S and COS in the gasifier. These species, along with CO_2, are separated from the gasifier off gas in the Rectisol unit and sent to the sulfur recovery plant. Claus or Stretford units will be used individually or in combination in the sulfur recovery plant depending on the sulfur content of the raw coal. To reduce the HC and CO levels to 100 ppm and the SO_2 levels to 250 ppm, incineration followed by SO_2 scrubbing may be required on sulfur plant tail gas. This

TABLE 2b. ANALYTICAL TEST PLAN FOR CASINGS RECEIVED FROM A LOCAL CERTIFICATED FACILITY (REV. 3)

Location to be sampled	Analysis to be performed															
	X	X									X	X	X			
	X	X									X	X	X			
	X	X	X	X	X						X	X	X			
	X	X									X	X	X			
		X				X	X	X			X	X	X	X	X	
		X				X	X	X	X		X	X	X	X	X	

TABLE 17. COMPARISON OF EMISSIONS ESTIMATES FOR 250 x 10^6 SCFD LURGI-BASED COAL GASIFICATION PLANTS (REF. 33)

Project	Emissions, lb/hr								
	Steam plant			Gasification plant			Total		
	SO_2	NO_x	HC	SO_2	NO_x	HC	SO_2	NO_x	HC
Northern Great Plains Resource Project (NGPRP) assuming compliance with applicable National Source Performance Standards (NSPS)	4,100	2,300	NR	1,300	310	10,300	5,400	2,600	10,300
Western Gasification Company (WESCO)	937	1,510	NR	130	105	4,100	1,067	1,615	4,100
Wyoming Coal Gas Company (WYCOAL)	3,074	1,057	NR	47	60	NR	3,121	1,117	NR
El Paso Gasification Project	60	67	NR	373	116	NR	313	153	NR

NR = Not reported.

TABLE 18. SUMMARY OF ESTIMATED HYDROCARBON EMISSIONS FOR A 250 x 10^6 SCFD GASIFICATION PLANT (REF. 33)

Hydrocarbon type	Emissions, lb/hr		
	Continuous	Fugitive	Total
CH_4	6,003	5	6,008
C_2 to C_3 paraffins	—	4	4
C_4+ paraffins	6.1	9	15.1
C_5+ aromatics	0.3	1.3	1.6
Olefins	3,634.5	6.8	3,641.3
Methanol	4.9	—	4.9
Isopropyl ether	0.6	—	0.6
TOTAL	9,649.4	26.1	9,675.5[a]

[a] NMHC = 3,673.

control technique or equally effective alternates may be required by State or Federal legislation.

The State of New Mexico has established emissions regulations for coal gasification plants (ref. 34). The U.S. EPA is preparing to propose regulations for new coal gasification facilities (Hedman, personal communication, October 1976). These regulations are compared in Table 19.

The types and quantities of gaseous emissions from coal gasification facilities remain poorly defined. The major sulfur-containing compounds emitted are expected to be H_2S, COS, and SO_2. Nitrogen-containing emissions are expected as NH_3, HCN, and NO_x. Hydrocarbon emissions may arise from both continuous and fugitive sources. The identity of the HOMC emissions is poorly defined; estimates can be made based on examination of engineering process flow and material balance estimates, pilot plant results, and by analogy to similar processes such as petroleum refining.

LIQUEFACTION

The objective of coal liquefaction processes is to convert solid coal into a liquid fuel and under certain conditions into gaseous fuels and useful byproducts. The liquefaction process involves cracking the coal molecular structure and either adding hydrogen or removing carbon to form a liquid. This is usually accomplished at high temperature and pressure. Liquefaction processes may be categorized into two groups.

1. Pyrolysis-based processes rely on thermal cracking with the removal of carbon to increase the hydrogen-to-carbon ratio, yielding liquids, gases, tars, and chars.
2. Dissolution processes involve the addition of hydrogen to free radical fragments of coal molecules formed in coal solubilization, thus increasing the hydrogen to carbon ratio and the ultimate liquid yield. These processes may or may not employ catalysts and may or may not be conducted in the presence of hydrogen.

Liquefaction of coal was used in Germany during World War II to produce over 15,000 BPD of aviation and motor fuels. The U.S. Bureau of Mines conducted research directed at gasoline and fuel production from 1944 to 1953. Although no commercial coal liquefaction facilities exist at present, research and development efforts in this area are receiving increased support. The

TABLE 15. REGULATIONS FOR COAL GASIFICATION PLANTS

Pollutant	State of New Mexico (Ref. 36)		EPA	
	Gas-fired power plant associated with coal gasification plants	Gasification plant	Power plants	Gasification plants[a]
Particulate	0.03 lb/10^6 Btu	0.03 gr/SCF	0.10 lb/10^6 Btu	NA
Sulfur dioxide	0.15 lb/10^6 Btu	NA	0.80 lb/10^6 Btu	500 ppm
Nitrogen oxides	0.30 lb/10^6 Btu[c]	NA	0.70 lb/10^6 Btu[c]	NA
Hazardous hydrocarbons	NA	NA	NA	0.005 lb/10^6 Btu, 100 ppm
Hydrogen sulfide	NA	10 ppm	NA	NA
Total sulfur	NA	0.900 lb/10^6 Btu	NA	0.033 $(A - B)^{0.5}$ lb/hr
Reduced sulfur (sum of H_2S, COS, and CS_2)	NA	100 ppm	NA	NA
Hydrogen cyanide	NA	10 ppm	NA	NA
Hydrogen chloride	NA	5 ppm	NA	NA
Ammonia	NA	25 ppm	NA	NA

[a]Proposed (Seldom, personal communication, October 1976).

[b]Based on oil-fired plant.

[c]Adopted as gas-burning equipment regulation.

NA = Not applicable.
A = Higher heating value of coal to gasifier, 10^6 Btu/hr.
B = Feed rate of coal sulfur to gasifier, lb/hr.

primary emphasis of these efforts is toward the production of environmentally acceptable substitutes for petroleum-derived liquid boiler fuels, with less emphasis on transportation fuels, distillate fuels, and chemicals. A major goal is the demonstration of the necessary liquefaction technology for commercial application by 1982-1985 (ref. 1).

Many liquefaction schemes are in various stages of development. Nine processes have been reviewed for the Electric Power Research Institute, (ref. 16) and a new process has been announced recently by Exxon (ref. 21). These processes are listed in Table 20. Several reviews (refs. 16,21,22,3,23) have described and compared many of these processes and also have reported their current status (ref. 1).

A wide range of operating conditions exists for the processes under consideration. Table 21 presents a summary of key operating parameters for four selected coal liquefaction processes. The type of reactor and the liquefaction temperature and pressure vary considerably depending on the process and the desired end products.

TABLE 20. COAL LIQUEFACTION PROCESSES (REF. 16)

Pyrolysis	FMC--COED Garrett--Flash Pyrolysis Oil Shale Corporation--TOSCOAL
Dissolution	
With hydrogen gas	
With catalyst	Hydrocarbon Research, Inc.--H-COAL U.S. Bureau of Mines (BOM)--Synthoil Gulf Research--Gulf Catalytic Coal Liquid
Without catalyst	Pittsburgh and Midway Co. (PAMCO) Solvent Refined Coal (SRC) Southern Services, Inc.--Solvent Refined Coal (SRC)
Without hydrogen gas	
With or without catalyst	Consolidation Coal Co.--Consol Synthetic Fuel Exxon--Exxon Donor Solvent (EDS)

TABLE 22. [illegible] AND OPERATING CONDITIONS FOR FOUR SELECTED LIQUEFACTION PROCESSES[a]

Process	Type	Temperature, °F	Pressure, psig	Reactor effluent	Principal products
[illegible][b]	Fluid bed pyrolysis	Stage 1, 350-600 Stage 2, 850 Stage 3, 1,250 Stage 4, 1,550°	0	Char, gas, liquid	Char, byproduct gas
[illegible][b]	Noncatalytic hydrogenation	840	1,000	Gas, char slurried in high boiling liquid	Fuel oil, naphtha
H-Coal[b]	Catalytic hydrogenation-ebullating bed	850	2,000	Gas, ash in liquid	Byproduct
SRC[c]	Noncatalytic donor solvent hydrogenation	370-420	1,500-2,500	Gas, liquid	Naphtha, fuel oil

[a]Values shown in this table depend on the original beans chosen; plant sizes as well as other factors differ and direct comparisons of the values is difficult.

[b]Ref. 21.

[c]Ref. 21.

Selection of the candidate processes "most likely to reach commercial status" is difficult. The processing conditions and the nature of the products formed in each of the alternate processes are so diverse that it is also difficult to select one flow diagram that would be representative of every process. Figure 5 presents a highly generalized coal liquefaction scheme and the required auxiliary facilities. The literature should be consulted to obtain details on the steps involved in any specific process.

Coal is first mined and transported to the liquefaction facility. This coal is then cleaned, crushed, dried, and either stored or fed directly to the liquefaction module. The variety of liquefaction processes and operating conditions was noted earlier (see Tables 20 and 21). The raw liquefaction product stream is separated into solids, liquids, and gases. Gaseous sulfur species in the raw product gas stream are separated in the acid gas removal module for subsequent sulfur recovery. The raw liquid product, after solids removal, is treated with hydrogen to reduce sulfur, nitrogen, and oxygen compounds and to hydrogenate unsaturated materials. The gas stream from hydrotreating is separated in the facility into a recyclable fuel stream and a stream rich in sulfur species for subsequent sulfur recovery. Hydrogen is required in the hydrotreating unit in many of the liquefaction schemes. Hydrogen production employs technology similar to that used in gasification processes.

Aside from the coal conversion module itself, many similarities exist between liquefaction and gasification operations. The types of auxiliary facilities required by each operation are almost identical. In addition, a coal gasifier may be included in liquefaction plants to provide makeup hydrogen and makeup fuel gas. These support and peripheral processes for liquefaction include the following:

1. Acid gas removal facilities for treating various acid (sour) gas streams,
2. A sulfur plant to recover sulfur as a byproduct from acid gas streams,
3. A power boiler and steam generator to supply the gasifier with steam,
4. A cooling tower,
5. A wastewater treatment facility with possible byproduct recovery,
6. A raw makeup water treatment facility, and

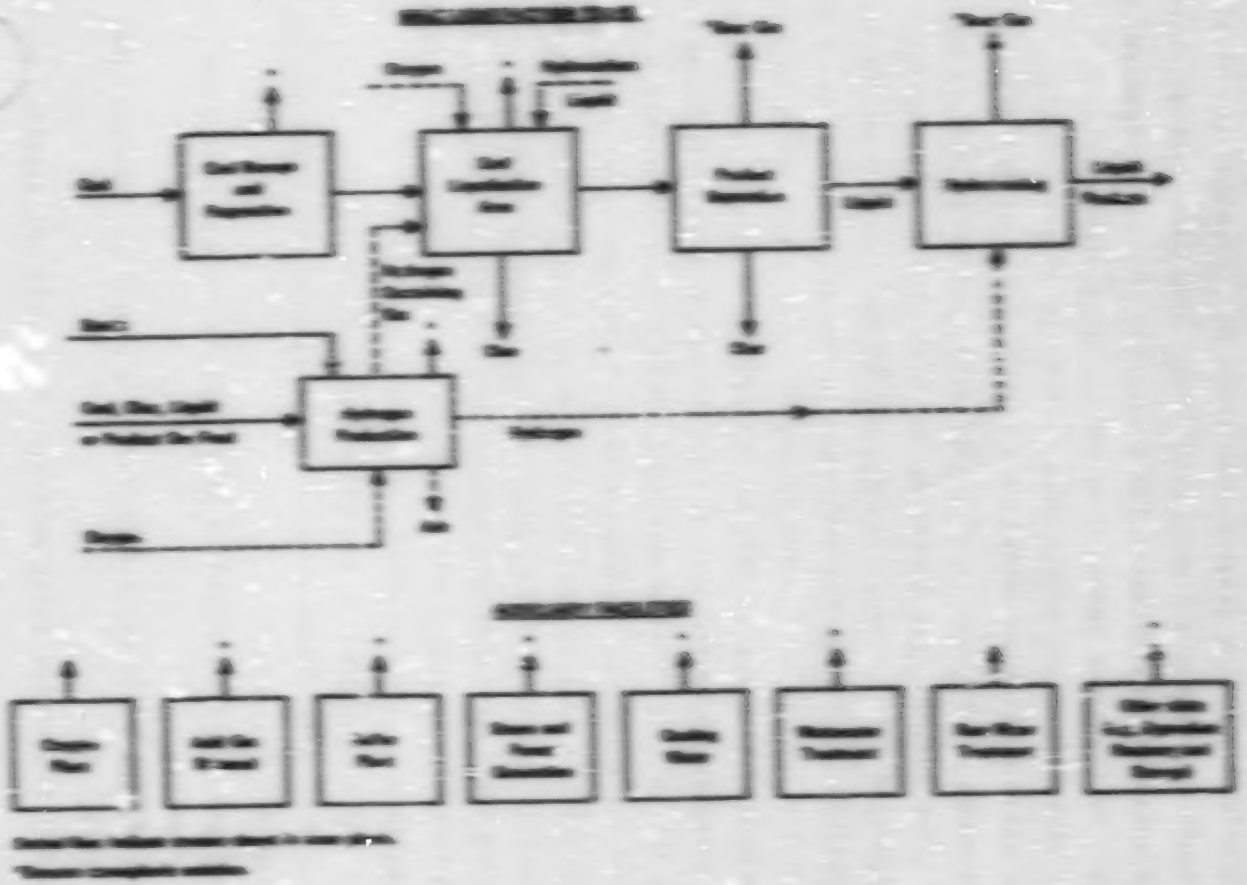

Figure 1. Generalized coal liquefaction scheme (ref. 22).

7. An oxygen plant to provide the gasifier or the liquefaction reactor with oxygen.

The liquid product from hydrotreating may be suitable for direct use as fuel or for refining into other products. Table 14 allows a comparison of sulfur and nitrogen contaminant concentrations in selected synthetic liquid products with those of the parent coal. Sulfur and nitrogen contaminants are converted primarily to H_2S and NH_3 in the liquefaction and subsequent hydrotreating processes. The contaminant level in the liquid product will depend on the severity of the hydrotreating process.

Although several sulfur species have been determined in liquid coal product, few analyses for nitrogen species have been conducted. This was noted in an earlier section on fuel contaminants in liquid coal product. The surveyed literature reveals only a single determination of trace gaseous species in gas streams from liquefaction facilities, a gas chromatographic analysis of raw pyrolysis gas and stack gas from the COED pilot plant (ref. 13). Over 100 components were observed; benzene and toluene were identified as prominent constituents. Table 33 depicts the concentrations of the quantified trace species from the above study and allows a comparison with the reported major gaseous species from the COED (ref. 14) and Synthoil (ref. 35) processes.

Expected atmospheric emissions sources for a liquefaction facility include the following:

1. Coal handling and pretreatment,
2. Vent gases,
3. Acid gas removal,
4. Sulfur recovery (tail gas),
5. Byproduct recovery and storage,
6. Cooling tower (from possible contamination of cooling water by leaks in heat exchange equipment),
7. Wastewater treatment,
8. Steam boilers (power generation) and process heaters and furnaces, and
9. Fugitive emissions (at valves, flanges, seals, pumps, compressors, and other equipment).

An analytical test plan (ref. 32) has been proposed to enable the assessment of the pollution potential of a COED coal liquefaction facility. This

plan, as shown in Table 23, reflects the anticipated distribution of various major air pollutants among the expected sources in a liquefaction facility.

The types and quantities of gaseous emissions from coal liquefaction facilities are poorly defined. The major sulfur-containing emissions are expected to be H_2S, COS, and SO_2. Nitrogen-containing emissions are expected as NH_3, HCN, and NO_x. Hydrocarbon emissions may arise from both continuous and fugitive sources. The identity of the BTEX emissions is poorly defined; estimates can be made based on examination of engineering process flow and material balance estimates, pilot plant results, and by analogy to similar processes such as coal gasification and petroleum refining.

SHALE OIL PRODUCTION

Oil shale is a type of sedimentary rock that is rich in organics. These mineralized organics are derived mainly from algae, spores, and pollen. The insoluble organic matter is known as kerogen and the soluble matter as bitumen. Considerable quantities of oil are released on subjecting this shale to destructive distillation at low pressure in a closed retort system. A yield of 10 gallons of oil per ton of shale is generally considered to be the minimum for commercial recovery by retorting techniques.

A major oil shale formation in the United States occurs along the Green River of Colorado, Wyoming, and Utah. Estimates of high-grade shale resources (greater than 30 gallons per ton) equivalent to 600 billion barrels of oil have been made for the Green River formation (ref. 36). Current shale oil production projections of 400,000 barrels per day by 1985 indicate that shale oil will assume a small share of the total energy requirement, reducing the quantity of imported oil by less than 1 percent (ref. 7). By the year 2000, however, shale oil could reduce foreign imports by up to 7 percent.

Several steps are involved in converting raw shale to products. The ore is first mined, and then is must be handled and treated prior to retorting. The shale is fed to the retort where the organic vapors are driven off at temperatures in excess of 450° C. Collected liquid and gaseous organic products must be upgraded to gaseous fuels, liquid fuels, and solids by various processes. The upgrading facilities will be similar to those downstream from the atmospheric distillation column in petroleum refineries. The spent shale solids present an enormous refuse disposal problem.

TABLE 23. [illegible]

[illegible]	[illegible]														
	x	x	x	x	x					x	x	x			
	x	x	x	x	x					x	x	x			
	x	x	x	x	x					x	x	x			
	x	x	x	x	x					x	x	x			
	x	x	x	x	x					x	x	x			
	x	x	x	x	x					x	x	x			
	x	x	x	x	x					x	x	x			
	x	x	x	x	x					x	x	x			
	x	x	x	x	x					x	x	x			
	x	x								x	x	x			
		x			x	x	x	x		x	x	x			x
		x				x	x	x	x	x	x	x	x		x

[illegible]

Several processes have been developed for shale oil production (refs. 36,37,38). Most of these involve the above-ground surface processing of the raw shale, i.e., TOSCO II, Lurgi-Ruhrgas, Union Oil, Bureau of Mines, Development Engineering, Petrosix, and Institute of Gas Technology. Occidental Petroleum, however, has developed an in situ process involving an underground retorting technique.

The TOSCO II process is the closest to commercial status and is likely to be employed in first-generation shale oil production plants (refs. 38,39). Discussion of air pollutant emissions is therefore limited to this process. In the TOSCO II process, crushed oil shale is heated to 480° C by direct contact with heated ceramic balls. The organic material in the shale rapidly decomposes to produce organic vapors. Cooling of the vapor yields crude shale oil and light organic vapors. A flow diagram depicting this process is presented in Figure 6.

Typical analyses of retort gas from a TOSCO-type process are presented in Table 24. It is anticipated that the retort gas will undergo desulfurization before use as a fuel. In addition, hydrotreating processes will be employed to upgrade the crude shale oil by removing nitrogen and sulfur with recovery as ammonia and sulfur.

Various types of pollutant emissions may be associated with shale oil processing: vehicular emissions from mining, construction, and transporting equipment; particulate emissions from shale handling; and gaseous emissions from retorting and subsequent refining operations. Expected atmospheric emissions sources for a shale oil facility include the following:

1. Oil shale handling and pretreatment,
2. Oil shale pyrolysis and shale oil recovery,
3. Vent gases from a variety of combustion sources (e.g., coking, hydrotreating, and hydrogen production),
4. Acid gas removal,
5. Spent shale moisturizer and disposal,
6. Sulfur recovery (tail gas),
7. Byproduct recovery and storage,
8. Cooling tower,
9. Wastewater treatment,

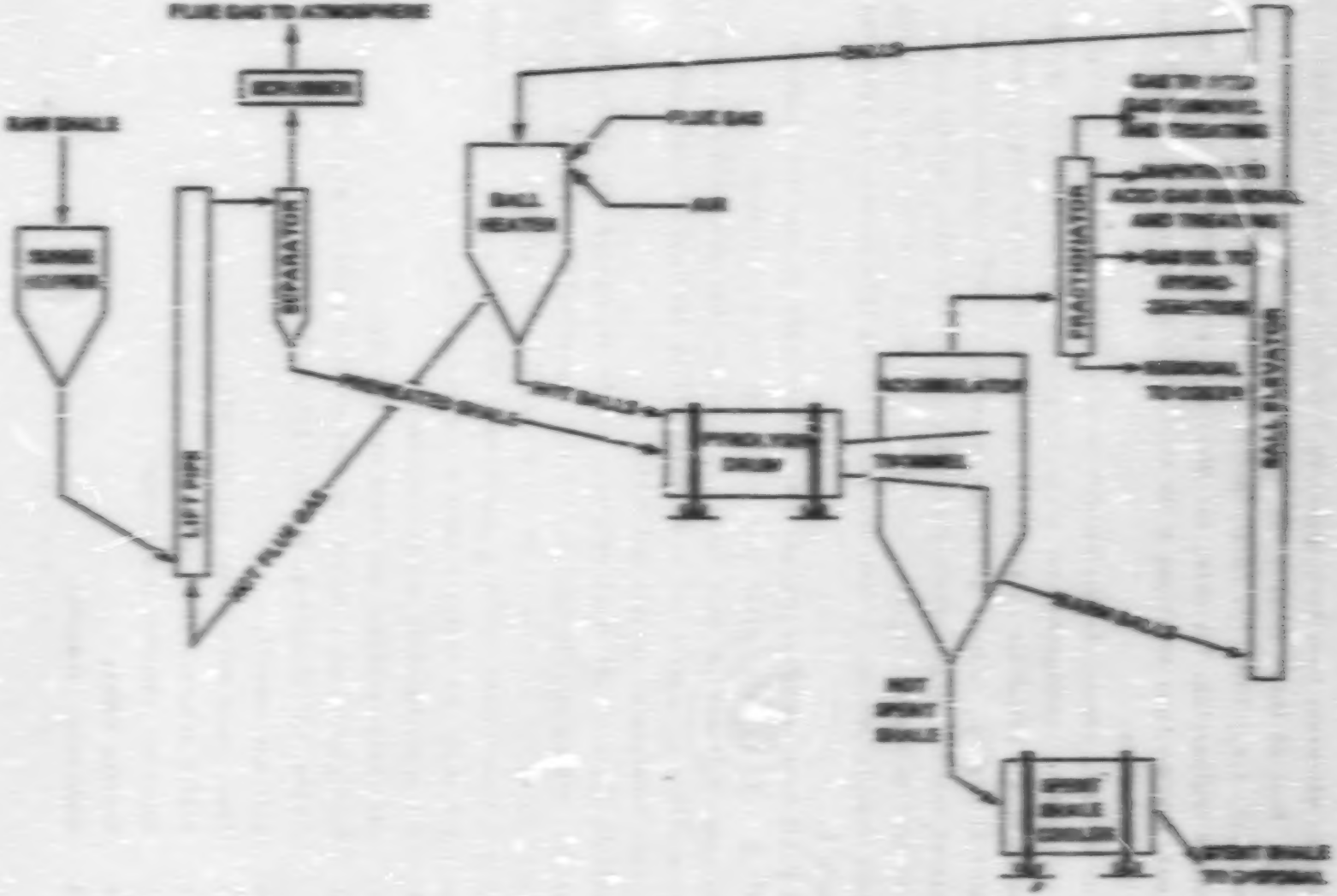

Figure 4. Tosco II process (ref. 40).

TABLE 24. TYPICAL RETORT GAS ANALYSES

	Volume %	
Methane	17.5[a]	15.2[b]
Ethane	7.0	10.3
Propane	3.4	4.0
Butanes	1.7	1.6
Pentanes (and higher)	1.0	c
Ethylene	8.2	5.4
Propylene	2.6	3.7
Butenes	1.9	2.7
Pentenes (and higher)	2.2	5.4[c]
Carbon Monoxide	2.0	3.6
Carbon Dioxide	30.3	11.4
Nitrogen	2.0	—
Hydrogen	23.9	22.4
Hydrogen Sulfide	2.3	4.3

[a]Ref. 41.

[b]Ref. 40.

[c]The 5.4 percent represents the sum of C_5 and higher alkanes and olefins.

10. Steam boilers (power generation) and process heaters and furnaces, and
11. Fugitive emissions (at valves, flanges, seals, pumps, compressors, and other equipment).

A generalized flow diagram depicting emissions sources is illustrated in Figure 7. Estimates of broad classes of controlled emissions from a 100,000 BPD TOSCO II facility are presented in Table 25. The results of Table 25 are compared in Table 26 with estimates from other sources (refs. 42,43). The agreement is good for the hydrocarbon emissions estimates, while the agreement is poorer for the estimates of pollutant emissions.

The estimates in Table 25 and 26 consider only continuous emissions. Three types of emissions may be associated with a shale oil facility: continuous, fugitive, and intermittent. Recent estimates (ref. 33) based on petroleum

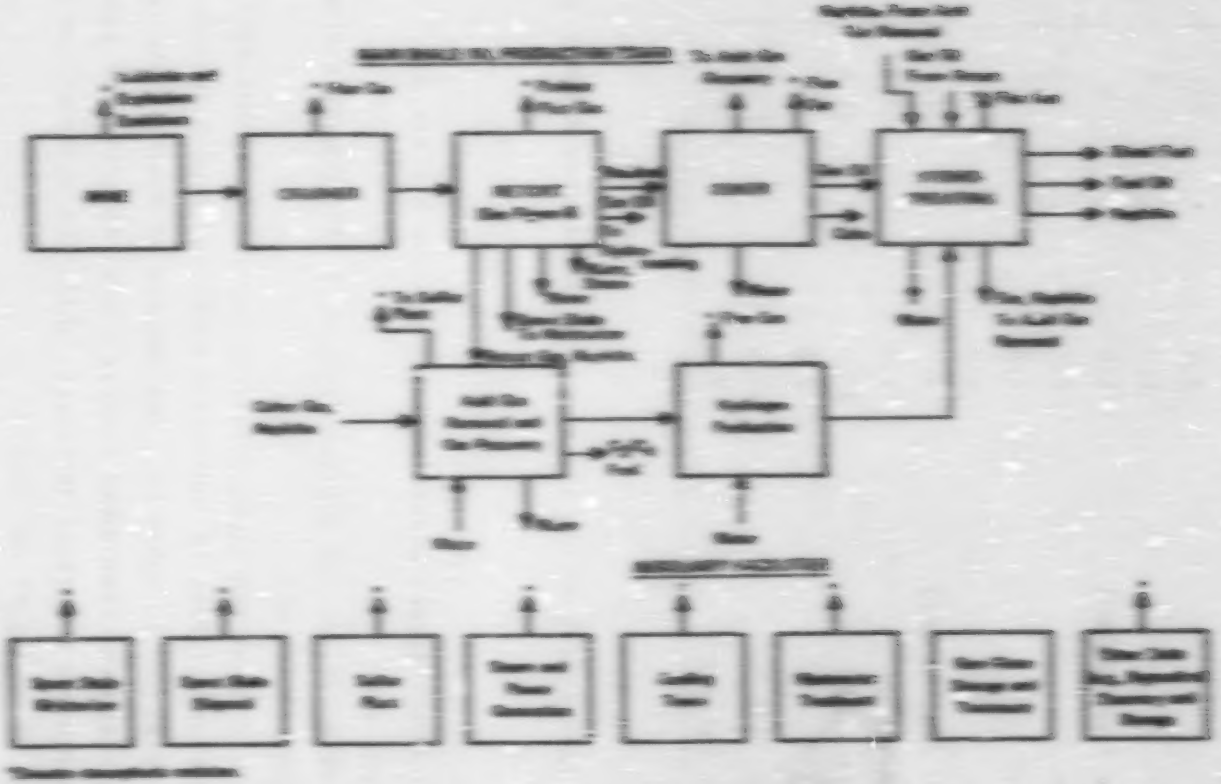

Figure 1. Generalized data oil production scheme.

TABLE 25. EMISSION RATES FOR 100,000 BPD TOSCO II FACILITY WITH EMISSIONS CONTROLLED WITH BEST AVAILABLE TECHNOLOGY (REF. 39)

Unit	Emissions, lb/hr			
	Particulates	SO_2	HC	NO_x
Ore Storage	36	---	---	---
Crusher	190	---	---	---
Raw Shale Preheat	419	2038	600	2355
Delayed Coker	3	90	---	150
Naphtha Hydrogenation	---	10	---	18
Gas Oil Hydrogenation Feed Heater and Fired Reboiler	3	36	---	158
Hydrogen Plant	31	643	---	1074
Spent Shale Moisturizer	44	---	---	---
Sulfur Plant	---	139	---	---
Utility Boilers and Steam Superheaters	108	190	---	321
TOTAL EMISSIONS, lb/hr	814	3134	600	4076

TABLE 26. COMPARISON OF EMISSIONS ESTIMATES FOR 100,000 BPD TOSCO II FACILITY[a]

Reference	Emissions, lb/hr			
	Particulates	SO_2	HC	NO_x
39 (Table 25)	814	3,134	600	4,076
42	9	1,688	548	394
43	1,482	2,660	631	2,920

[a]Emissions have been scaled up linearly from estimates for a 50,000 BPD facility.

refinery operations have considered all these categories and, in addition, have categorized the hydrocarbon emissions according to hydrocarbon type. These results are shown in Table 37.

The total continuous emissions estimate agree with estimates for hydrocarbons presented in Table 36. Intermittent and fugitive emissions categories are estimated to contribute substantially (73 percent) to the total hydrocarbon emissions. Photochemically reactive species are estimated to be emitted in large quantities. Olefins, for example, account for 30 percent of the total emissions. Derivatives including the thiols, are estimated to account for only 0.1 percent of the emissions.

In addition to the emissions from shale oil processing facilities, gaseous organics may be released from the large volume of spent shale solids (ref. 36). Considerable quantities of polycyclic organic matter (POM) may be present on the spent solids, and the release of both unsaturated and saturated hydrocarbons up to C_{25} has been demonstrated. The POM is probably sorbed from the retort vapors on the shale solids prior to solids removal from the retort. Carcinogenic species such as 3-methylcholanthrene, 7,12-dimethyl benz[a]anthracene, and benzo[a]pyrene, in addition to noncarcinogenic compounds such as phenanthrene, fluoranthene, pyrene, and perylene, have been identified in spent shale solids. Volatile alkanes and olefins as well as POM may be released from spent shale solids by evaporation or auto-oxidation processes. Emissions data are lacking, which would allow assessment of this source on local air quality. The carcinogenicity of various POM presents an additional potential airborne hazard from shale oil facilities.

The types and quantities of emissions from shale oil facilities remain poorly defined. Although many of the complex sulfur- and nitrogen-containing compounds may be emitted by shale oil facilities, better definition of process conditions is needed before extrapolations to commercial facilities can be made.

PETROLEUM REFINING

Crude oil is a mixture of many hydrocarbons: paraffins, naphthenes and aromatics (ref. 44). The chemical composition of the crude is strongly dependent on the geological formation of origin. The physical appearance of the crude may range from tar-like to almost clear.

The general objective of petroleum refining is to separate the crude oil into various fractions, which can be subsequently converted, treated, and blended into finished products. Five broad types of refineries are classified below according to their specific objectives (ref. 45):

1. Topping,
2. Fuel oil,
3. Gasoline,
4. Lube oil, and
5. Petrochemical.

In 1976, 253 refineries in the United States processed 13.7 million barrels per day (BPD) of crude oil (ref. 44). This amounts to a mean production of 50,000 BPD per refinery. Newer facilities, however, have capacities in excess of 100,000 BPD. Figure 8 represents a generalized flow diagram for a hypothetical 100,000 BPD petroleum refinery. The refinery product yields, depicted in this diagram, are representative of 1974 United States production averaged across all refineries.

In addition to the auxiliary operations, refining operations generally include the following four major steps (ref. 44):

1. Separation processes, such as atmospheric and vacuum distillation and acid gas removal;
2. Conversion processes, such as catalytic cracking, reforming, light hydrocarbon processing, isomerization, coking, hydrocracking, and desulfurization;
3. Treatment to remove sulfur and other undesirable components from selected streams; and
4. Blending and storage.

The auxiliary operations include such processes as crude desalting, hydrogen generation, sulfur recovery, water cooling, water treatment, and power generation. Many of the individual processes are depicted in Figure 8. Detailed descriptions of these operations are beyond the scope of this report. Specific process information, however, can be found in the literature (refs. 44,45,46) and the references therein.

All of the above facilities are potential sources of atmospheric emissions. Considerable quantities of emissions are released by combustion of fuel-rich gas streams produced by individual process units, regeneration of catalyst from

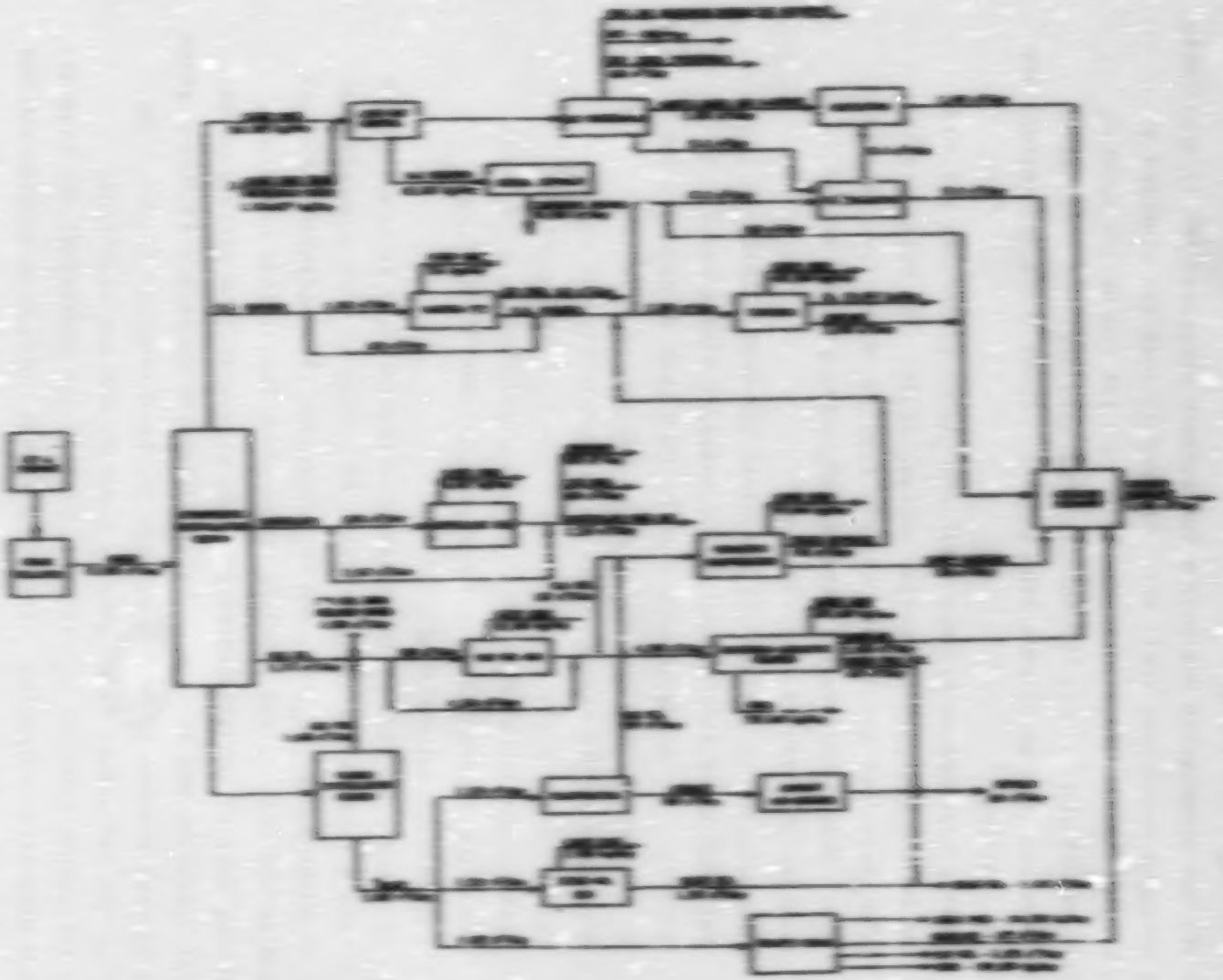

Figure 1. [illegible] for a representative U. S. petroleum refinery (ref. 40).

the fluid catalytic cracker (FCU); and evaporation and breathing losses from storage tanks. Miscellaneous or fugitive sources include loading facilities, sampling, spillage, and leaks.

The EPA has promulgated New Source Performance Standards (NSPS) applicable to three refinery operations (ref. 47). The regulations are directed at limiting sulfur dioxide (SO_2) emissions from fuel gas combustion systems, particulate matter and CO from FCU catalyst regenerators, and hydrocarbon emissions from the storage of petroleum liquids. These three regulations are summarized as follows.

1. Refinery processes produce large quantities of process gas rich in both organics and hydrogen sulfide (H_2S). The NSPS requires that this fuel gas contain no more than 230 mg/m^3 (163 ppm) of H_2S. This effectively limits the SO_2 concentration in the combustion products to 15-20 ppm.
2. The quantity of particulate emissions has been limited to 1 kg/1,000 kg of coke burned in FCU catalyst regeneration. In addition, the plume opacity must be less than 30 percent, the CO content of the stack gas must be 500 ppm or less.
3. Petroleum liquid storage vessels with capacities of 40,000 gallons or more are required to have certain types of tank designs or control equipment to reduce hydrocarbon emissions. The exact type of equipment required depends on the vapor pressure of the stored liquid.

Emissions estimates for five of the criteria pollutants may be compared for a gasoline and a fuel oil refinery in Table 28. This listing suggests that the bulk of particulate, SO_2, CO, and NO_x emissions is associated with fuel combustion in the heaters and furnaces employed in the various processes. Hydrocarbons, however, are indicated to arise primarily from miscellaneous (fugitive) emissions and storage. The miscellaneous emissions estimates given in Table 28 were assumed to be 0.1 percent of the throughput weight. The identity of the individual hydrocarbons, however, was not specified.

The literature provides little definition of the individual air contaminants from petroleum refineries. This is somewhat surprising considering the current well-developed state of petroleum-refining technology. The EPA is planning an intensive measurement program to identify and quantify emissions

TABLE 33. [illegible]

[illegible]	[illegible]									
	[illegible]					[illegible]				
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]

of individual chemical species from petroleum refineries. Some of the preliminary work includes a recent report which defines sampling and analytical strategies for quantifying specific hazardous components in petroleum refinery effluents (ref. 46). According to Dale Denny, EPA, Research Triangle Park, N.C., actual analytical results should be available by late 1977 or early 1978 (personal communication, 1976). Until this comprehensive measurement program has been completed, specific emissions estimates must be based on the scattered analyses of intermediate process streams and final products reported in the literature.

A characterization of the atmospheric emissions from three refinery operations was attempted recently using reported process stream analyses. The three operations include the atmospheric crude still, the fluid catalytic cracking regenerator, and the sulfur recovery unit. Results from this study are shown in Table 29 and depict major and minor constituents identified in process streams from each operation. Species reported as "potentially present" were not included. Atmospheric emissions from these processes should be of similar composition as the process streams.

A list has been compiled (ref. 46) of some 475 compounds found in one or more of 13 selected intermediate petroleum refinery process streams. Table 30 lists the classes of compounds and the corresponding number of individual species identified or quantified in this survey. For details concerning streams, species, and concentrations, the referenced report should be consulted.

The composition of process streams intermediate in the production of the final products was examined above. Analyses of the final products from petroleum refining should provide insight into the identity and amounts of miscellaneous and storage emissions from these products. Gasoline, a major product, is blended, and its composition depends on the season, climate, and location of the intended market. Analyses of gasoline liquid have been reported by several workers (refs. 48,49,50). Comprehensive analyses of up to 330 hydrocarbons have been reported for gasoline liquid and vapor (ref. 48). Alkanes are reported as the dominant class of hydrocarbons in gasoline vapor, making up to 85 percent of the total. The effects of recent requirements for

TABLE 79. [illegible] (Cont.)

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]						[illegible]	
[illegible]						[illegible]	
[illegible]	[illegible]						
[illegible]	[illegible]						
[illegible]	[illegible]						
[illegible]	[illegible]						
[illegible]	[illegible]						
[illegible]	[illegible]						
[illegible]	[illegible]						
[illegible]	[illegible]	[illegible]					
[illegible]	[illegible]						
[illegible]		[illegible]					
[illegible]		[illegible]					
[illegible]						[illegible]	
[illegible]			[illegible]	[illegible]			
[illegible]			[illegible]				
[illegible]						[illegible]	

[redacted]

TABLE 30. CLASSES AND NUMBERS OF COMPONENTS IDENTIFIED IN REFINERY STREAMS (REF. 46)

Acids and anhydrides	57	Hydrocarbons	
Amines	2	Aliphatics	94
Ketones and aldehydes	3	Olefins	33
Combustion gases	13	Aromatics	88
Heterocyclics		Phenols	30
Pyridines	25	Polynuclear aromatics	19
Pyrroles	1	Polynuclear azo arenes	36
Cyclic sulfides	25	Thiols (mercaptans)	29
Bicyclic sulfides	13	Sulfides	24
Thiophenes	14	Cyanides	2

lead-free gasoline have precipitated compositional modifications by petroleum refiners, which are unclear at this time. In any event, caution should be observed in using the reported results for estimating hydrocarbon emissions from miscellaneous sources or gasoline storage.

The types and quantities of gaseous emissions from petroleum refineries are poorly defined. The surveyed literature indicates the major sulfur-containing emissions to be SO_2, H_2S, and thiols, while major nitrogen-containing emissions include NO_x and NH_3. Although the individual hydrocarbons emitted from petroleum refineries have not been reported based on actual analyses, the major organic emissions are likely to be highly volatile compounds, C_{10} and lower. Compositional analyses are available for various intermediate process streams and final products. This information can be used in conjunction with vapor pressure data and established emission factors (ref. 51) to estimate atmospheric emissions from various process modules. This type of theoretical source reconciliation of individual species is difficult due to the fugitive nature of the majority of hydrocarbon emissions and due to the limited data base. Comprehensive source and ambient sampling surveys will be required to verify these estimates.

OVERVIEW

Fuel conversion industries include coal gasification, coal liquefaction, shale oil processing, and petroleum refining. Although the fuel conversion technology is markedly different in these facilities, many of the same well-proven operations and processes will be integrated into each fuel production facility. Table 31 summarizes many of the processes expected to be required in each fuel production facility. These processes also represent potential sources of atmospheric emissions from fuel production. Comparison of the processes in Table 31 suggests that quantification of the emissions from many petroleum-refining operations can provide a data base for estimation of a sizable fraction of the atmospheric emissions from other fuel conversion industries.

Major sources of atmospheric emissions from fuel conversion facilities are expected to include various combustion operations and miscellaneous (or fugitive) emissions. Quantitative atmospheric emissions estimates are available for criteria air pollutants. Table 32 presents a compilation of emissions estimates from fuel extraction and conversion modules as reported in or calculated from the literature. Although a common basis of 10^{12} Btu/day of fuel output was used, the results are not truly comparable because the final products are not identical in each case. These results can be summed along with other related emissions estimates (such as from transportation of raw fuel and ultimate combustion of final products) to assess the total emissions impact on the atmosphere resulting from utilization of each alternative fuel. Caution should be exercised in using these first-generation estimates since an appraisal of their accuracy is currently lacking.

A broad spectrum of sulfur-containing compounds, nitrogen-containing compounds, and hydrocarbons has been identified from analyses of intermediate process streams and final products from fuel conversion processes. The surveyed literature provides a basis for indicating the major anticipated compounds. The same or similar species are expected to be emitted from each fuel conversion facility. These compounds are listed as follows:

1. Sulfur-containing compounds will include SO_2, H_2S, thiols (mercaptans), sulfides, and thiophenes.
2. Nitrogen-containing compounds will include NO, NO_2, NH_3, HCN, and heterocycles.

TABLE 31. POTENTIAL SOURCES OF ATMOSPHERIC EMISSIONS FROM FUEL CONVERSION FACILITIES

Source	Coal gasification	Coal liquefaction[a]	Shale oil production	Petroleum refining
Coal mining and preparation	X			
Gasifier	X			
Hydrogen production (shift reactor)	X	X	X	X
Quench and scrubbing unit	X			
Acid gas removal	X	X	X	X
Methanation	X	X	X	X
Liquefaction unit		X		
Product separation		X	X	X
Hydrotreating		X	X	X
Oil shale mining and preparation			X	
Retort			X	
Coker			X	X
Crude desalting				X
Atmospheric and vacuum distillation				X
Catalytic cracking				X
Catalytic reforming				X
Light hydrocarbon processing				X
Isomerization				X
Hydrocracking				X
Oxygen plant	X			
Sulfur plant (tail gas)	X	X	X	X
Steam and power generation (fuel combustion)	X	X	X	X
Process heaters (fuel combustion)	X	X	X	X
Cooling towers	X	X	X	X
Waste water treatment	X	X	X	X
Boiler water treatment	X	X	X	X
Byproduct recovery	X	X	X	X
Blending	X	X	X	X
Storage	X	X	X	X
Flare gas (startup, shutdown, and upset conditions)	X	X	X	X
Miscellaneous (fugitive) sources	X	X	X	X
Spent shale moisturizer			X	
Spent shale disposal			X	

[a] It is assumed that a gasification unit is not included with the liquefaction facility.

TABLE 32. ESTIMATED ATMOSPHERIC EMISSIONS FROM FUEL EXTRACTION AND CONVERSION OPERATIONS ON A BASIS OF 10^{12} BTU/DAY OUTPUT

Operation	Pollutants	Emissions, lb/hr			
		SO_x	CO	NO^a	NO_x
Extraction[b]					
Gas well production	0	1,071	0	1,100[c]	1,833
Oil well production	417	536	267	550	917
Coal strip mining, active[d]	520 (1,040)	115 (230)	20[e] (130)	10[e] (1,000)	120[e] (1,000)
room and pillar[d]	260 (5,000)	460 (8,800)	33 (630)	5 (1,000)	460 (8,800)
Shale mining, surface	1,111	75[e]	500[e]	1,000	1,667
room and pillar	556	38	250	50	833
Conversion					
Petroleum refining[b]	513	1,317	513	2,722	1,833
Coal gasification[f]	2,000	8,000	800	66,133	8,000
Shale oil production[g]	1,875	2,143	833	3,000	4,000
Extraction plus conversion					
Gas	0	1,071	0	1,100	1,833
Petroleum	560	1,853	317	3,083	2,333
Coal (gasification)[f]	1,156	8,115	833	66,156	8,000
Shale oil[g]	2,019	2,218	1,083	3,139	5,000

[a] In each case that showed a clear distinction, the hydrocarbon emissions estimate are as nonmethane hydrocarbons (NMHC).

[b] Ref 55.

[c] Methane emissions are not included; emissions estimates including methane are 11,000 lb/hr.

[d] Emissions in parentheses include emissions from physical coal cleaning.

[e] Emissions result primarily from vehicular activities in the extraction operation.

[f] Emissions in parentheses include emissions from burning refuse piles.

[g] Methane emissions are not included; emissions estimates including methane are 15,667 (15,701 lb/hr.

[h] Ref. 15; emissions estimates are scaled from a 100,000 BPD gasoline refinery.

[i] Hydrocarbon emissions estimates are scaled from the sums of the values reported in Table A2; hydrocarbon estimates are scaled from the sums of the NMHC values reported in Tables A2 and A3; utilities are scaled from estimates for a 410 x 10^6 Btu/hr facility consuming 1 coating value of 1,000 Btu/SCF for the product SNG.

[j] Hydrocarbon emissions estimates are scaled from the sum of the values reported in Table D8; nonmethane hydrocarbon estimates are scaled from the value reported in Table J1; the assumed heating value of shale oil is 5.0 x 10^6 Btu/bbl.

[k] NR = not reported.

[l] Coal is assumed to be extracted with physical cleaning; although particulate and CO emissions were not reported for gasification facilities, values for petroleum refining have been adopted.

[m] Shale is assumed to be mined by room and pillar techniques; although no emissions were not reported for shale oil production facilities, values for petroleum refining have been adopted.

3. Organic compounds will include primarily volatile hydrocarbons up to C_{10}. Other organics such as aldehydes, ketones, phenols, and POM are expected. The carcinogenicity of various POM presents an additional airborne hazard.

The extent to which any of these species is released to the atmosphere is unclear at this time and depends to a large degree on currently undefined processing details. Comprehensive source and ambient surveys will be required to identify and quantify gaseous emissions from fuel conversion facilities.

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